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JULY 30, 1990

CHEMICAL & ENGINEERING

NEWS

udy reveals members' views
of ACS products and services
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Photosynthetic Reaction Centers

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CHEMICAL & ENGINEERING NEWS

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JULY 30, 1990

News of the Week

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■ **French group develops copper complexes that mimic the double-helical structure of DNA but turn it "inside-out," offering a way to gain more insight into this biological linchpin.** **Page 7**

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■ **Hearing on July 5 blast at Arco plant in Texas includes calls for better management-worker communication, defense of using contract workers.** **Page 8**

Cover: Argonne National Laboratory's computer-generated diagram of photosynthetic reaction center in *Rhodobacter sphaeroides R-26* embedded in bilayer membrane

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Science/Technology

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Scanning tunneling microscope grabs the sharpest DNA image achieved to date. **Page 20**

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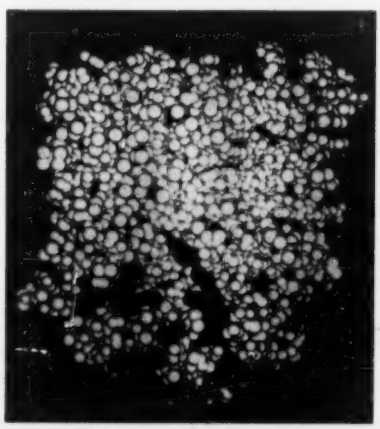
"Forty years of Firsts: The Recollection of a Dow Corning Pioneer" by Earl L. Warrick pays homage to silicone's development and other Dow history. **Page 38**

ACS News

ACS members generally are satisfied with the society's products and services, and supportive of its goals, a survey finds. **Page 42**



Special Report

Chemistry of photosynthesis in purple photosynthetic bacteria begins in membrane-embedded reaction centers, which offer model systems for studying photosynthetic conversion. **Page 22**

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LETTERS

CHEMICAL SAFETY

Tantalum amide preparation

Explosions in two laboratories have prompted us to comment on the preparation of pentakis-dimethylamido tantalum, $Ta(NMe_2)_5$. The original paper by D. C. Bradley and M. Thomas [*Can J. Chem.*, 40, 1355 (1962)] provides a procedure for the synthesis of the compound, which if strictly followed does not give the desired product. The procedure given directs one to add $TaCl_5$ to a slurry of $LiNMe_2$ in pentane.

If one has rigorously purified the $LiNMe_2$ and is careful to exclude moisture, little reaction occurs. One is left with a finely divided mixture of $LiNMe_2$ and $TaCl_5$, which sometimes detonates during routine manipulation.

This can be avoided by preparing the $LiNMe_2$ in situ, being careful to use excess $HNMe_2$. It appears that the reaction progresses initially by reaction of the $TaCl_5$ with the amine [Chisolm, M. H., Huffman, J. C., Tan, L.-S., *Inorg. Chem.*, 20, 1859 (1981)], with the last two or three dimethylamide groups being metathesized onto the tantalum center by the $LiNMe_2$. The reaction has also been found to proceed smoothly to the desired product if a pentane/diethyl ether solvent mixture (50-50) is used.

Robert W. Chestnut
Ian P. Rothwell
Purdue University
Mark Banaszak Holl
Peter T. Wolczanski
Cornell University

Career decisions

Convincing arguments can be made for the desirability of increasing financial support for chemistry students in college and graduate school and for teaching and research equipment, but it seems to me quite unproven that such increased support would increase significantly the number of students who become chemists.

Is it really true that students decide to become chemists after they are in college and not earlier?

Is it really true that students deciding whether or not to become chemists are well informed about the financial rewards of various possible careers in chemistry and are influenced by such information?

Is it really true that significant numbers of capable students are dissuaded from careers in chemistry by large impersonal lecture courses in college general chemistry?

I know of no reason to believe any of these things. The first does not agree with the few studies I have seen and with my own limited observations; the second is highly implausible (where and from whom would students get such information?); and the third seems clearly untestable.

More information about when and why students make particular career decisions seems to me to be a better basis for action than assumptions, no matter how plausible and attractive they may be.

James Moffat
San Antonio

Plastics recyclable

In your product report on aerosols, (C&EN, April 23, page 35), you quoted "another industry source" as stating that "these packages . . . do add to the landfill problem. Unlike metal aerosol cans, the plastics they are made from are not recyclable." According to the article, the inner bottle is made of polyethylene terephthalate, "the same plastic used to make large soda bottles." This plastic has been recyclable for several years now. The outer container, which is probably made of other types of polyethylene, is also recyclable. My neighborhood has been collecting and recycling these plastics for four months now.

I think the nonaerosol packages are great, and it is not a disadvantage that they are made of plastic. Many plastics are recyclable, which is a fact that needs more publicity.

Sharon R. Camp
Mableton, Ga.

Keeping a civil tongue

In Ron Dagani's balanced report (C&EN, April 16, page 28) on the 1st Annual Conference on Cold Fusion in Salt Lake City, I read that "the skeptics were taunted from the podium in much the same way that cold fusion pioneers B. Stanley Pons and Martin Fleischmann were ridiculed last May at an American Physical Society meeting in Baltimore."

I remember well the reports on the Baltimore meeting, and my disgust and

SECOND-QUARTER EARNINGS: Results show little pattern

The immediate future of the economy seems to be a mystery to the experts these days, and equally so to those who follow the fortunes of the chemical industry. Second-quarter financial results for 16 chemical companies reporting so far range from sizable declines to respectable increases, with half of the companies having increases.

Dow Chemical, which set a goal a number of years ago of becoming less dependent on commodity chemicals with their up and down cycles, posted a year-to-year 50% earnings decline. Monsanto, which set the same goal, had an earnings increase of 2%. American Cyanamid, which, because of its big stake in pharmaceuticals, has usually been less cyclical than most chemical firms, registered earnings growth of 11% for the quarter. And specialties manufacturer Lubrizol posted a strong 27% earnings increase.

The biggest disappointment was Dow, whose earnings dropped to $364 million on a 4% sales increase to $4.81 billion. The result was that profit margins at the company fell to a more normal 7.6% in the second quarter this year from a whopping 15.8% in the same period in 1989.

Dow's decline evidently shook Wall Street, which will normally discount a stock for poor earnings prior to release of results. But in this case, Dow's decline—5¾ points, closing at 52⅜—on the New York Stock Exchange came only on the day its results were released.

The problems at Dow came primarily in two business segments—chemicals and performance products, and plastics. For the plastics unit, sales declined 3% to $1.8 billion, but operating income dropped 40% to $279 million. Pricing pressure in thermoplastics in June limited a recovery that had been seen earlier in the quarter, and higher costs and softening demand cut margins in thermosets.

In the chemicals and performance products segment, sales fell 12% to $1.2 billion, but operating income declined 63% to $177 million, partly as a result of chlor-alkali plant outages in Brazil and Canada.

Adding to the earnings decline were increases in nonoperating expenses such as interest. The company did benefit from its consumer specialties segment, for which sales rose 48% to $1.3 billion and operating income increased 46% to $268 million.

Of the 16 companies surveyed by C&EN, others whose earnings rose—besides Lubrizol, Cyanamid, and Monsanto—include W. R. Grace (15%), Ethyl (12%), Petrolite (10%), Air Products & Chemicals (7%), and Rohm & Haas (1%).

William Storck

Chemical company earnings performance varies widely in second quarter

	SECOND-QUARTER 1990						FIRST-HALF 1990					
			Change from 1989		Profit margin[b]				Change from 1989		Profit margin[b]	
$ Millions	Sales	Earnings[a]	Sales	Earnings	1990	1989	Sales	Earnings[a]	Sales	Earnings	1990	1989
Air Products	$ 712.8	$ 56.8	7%	7%	8.0%	8.0%	$1425.9	$111.1	7%	6%	7.8%	7.9%
American Cyanamid	1228.3	108.4	6	11	8.8	8.5	2380.8	205.3	5	17	8.6	7.8
Arco Chemical	705.0	102.0	−3	−15	14.5	16.5	1390.0	227.0	−2	−4	16.3	16.6
Dow Chemical	4807.0	364.0	4	−50	7.6	15.8	9707.0	826.0	7	−44	8.5	16.2
Ethyl	603.3	57.1	0	12	9.5	8.5	1210.0	109.6	3	7	9.1	8.7
Georgia Gulf	218.7	30.9	−25	−37	14.1	16.9	470.4	68.3	−23	−35	14.5	17.2
B. F. Goodrich	632.5	34.9	1	−34	5.5	8.4	1222.3	51.1	−2	−51	4.2	8.4
W. R. Grace	1628.5	51.3	8	15	3.1	3.0	3135.8	83.9	8	12	2.7	2.6
Hercules	795.8	30.2	1	−27	3.8	5.3	1567.2	63.9	2	−26	4.1	5.6
Lubrizol	357.8	33.1	9	27	9.2	7.9	715.0	62.2	6	10	8.7	8.4
Monsanto	2367.0	247.0	1	2	10.4	10.3	4653.0	441.0	1	−5	9.5	10.0
Olin	660.0	29.0	0	−17	4.4	5.3	1296.0	61.0	−2	−12	4.7	5.2
Petrolite	72.6	3.6	1	10	5.0	4.6	144.6	7.3	0	14	5.0	4.4
Rohm & Haas	768.5	70.0	5	1	9.1	9.4	1462.9	124.1	3	1	8.5	8.7
Union Carbide	2135.0	116.0	−6	−38	5.4	8.2	4308.0	210.0	−5	−46	4.9	8.6
Witco	403.3	18.5	−2	−20	4.6	5.6	798.6	33.0	−2	−18	4.1	5.0

a After-tax, excluding significant nonrecurring and extraordinary items. b After-tax earnings as a percentage of sales.

French group prepares copper complexes that resemble "inside-out" DNA

Copper complexes that mimic the elegant double-helical structure of DNA but turn the structure inside-out have been prepared for the first time by chemists at Louis Pasteur University in Strasbourg, France. The new molecules, while not themselves DNA, may enable scientists to gain insights into how it interacts with other molecules. Such studies could eventually lead to the development of new drugs that target DNA.

The new molecules, prepared by professor Jean-Marie Lehn and coworkers Ulrich Koert and Margaret M. Harding, consist of an organic "spiral staircase" curling around a column of three or five copper ions. The staircase is fashioned from two intertwined strands of a linear oligomer containing bipyridine units. Attached to each bipyridine unit and flaring outward is a pair of deoxynucleosides, such as deoxythymidine.

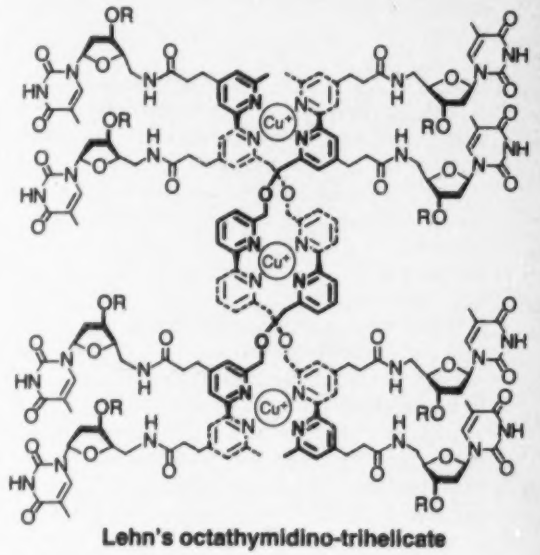
In DNA, the deoxynucleosides are inside the double helix and stacking interactions between them hold the two strands together. The overall charge of DNA is negative. In Lehn's molecules, by contrast, the deoxynucleosides are outside the helix and the stacking is between pyridines. The overall charge, due to the copper ions, is positive.

The structure of these so-called nucleohelicates is "strikingly reminiscent of Linus Pauling's original proposal for the structure of DNA," notes coordination chemist Edwin C. Constable of the University of Cambridge, U.K. That proposal, which was later shown to be incorrect, put the deoxynucleosides on the outside and the charged phosphate groups facing in.

Remarkably, the nucleohelicates assemble spontaneously when the bipyridine chains are allowed to interact with copper ions. Scientists aren't sure what drives this spontaneous assembly, although Constable thinks an important controlling factor is the stacking of coplanar pyridine rings.

Lehn has been studying such self-assembling helicates for years, but the new twist is the addition of nucleoside appendages. He says other groups can also be attached to the helix, such as amino acids, sugars, and electroactive and photoactive units.

Lehn's compounds may help shed light on the ways biological molecules are built up and how they recognize and interact with other molecules, Constable says. In particular, the nucleohelicates might be used to probe a new type of molecular recognition—"the recognition of one helix for another helix," he tells C&EN. They "might intercalate or enter into triple-helix hydrogen-bonding interactions with DNA," he notes in a companion article to Lehn's paper in last week's issue of *Nature* [**346**, 339 (1990)]. In addition, double-helical complexes with photoactive metal centers might be developed to target specific nucleic acid sequences on DNA, he says.



Lehn's octathymidino-trihelicate

R = tert-butyldimethylsilyl

Double-helical complexes, which are being studied by several other groups as well, might also be envisioned as a model for a molecular wire, Constable observes. Extended indefinitely, the complex essentially would be a metallic filament encased inside an organic insulator. At least that's "the way I think about it in grant proposals," Constable laughs.

Ron Dagani

Chemical industry in China on rebound

After hobbling through what one Chinese publication calls "a rough and turbulent time" last year and early this year, China's economy and industry and its foreign business ties show signs of bottoming out, according to official figures just issued. However, Chinese and U.S. sources caution, many serious problems remain.

Overall industrial output has started up, with monthly growth rates of 1.4, 2.0, 4.2, and 5.9% in March through June, compared with 1989, and 2.2% growth for the first half of 1990. This follows declines starting last October—down 0.9% in January and February, for example. Afflicted by an austerity program, major infrastructure deficiencies, and world reaction to the political crackdown that began in Beijing's Tiananmen Square on June 4, 1989, China's industrial output grew just 6.8% in 1989, only a third of the 1988 rate (C&EN, Feb. 19, page 6).

Chemical industry led the rebound with a 6.5% increase in the first half, three times higher than industry overall, after also stagnating in January and February. Reflecting the top priority China gives agriculture, fertilizer and pesticides made the most dramatic leaps. China produced 45.9 million metric tons (gross weight) of chemical fertilizer in the first half, up 8.4% from last year's first half, and 119,000 metric tons of pesticides, up 16%, exceeding plan targets by 2.7% and 6.7%, respectively. Of 16 major chemicals, 14 fulfilled their half-year goals.

Foreign investment also rose in May and June, following a decline in the second half of 1989 and through April this year. China approved 530 foreign-funded projects in May with promised foreign capital of $540 mil-

Ethylene Oxide/Glycol Profitability In Doldrums

Prices of oxide and derivatives drop as demand growth slows and supplies rise, spurring antifreeze and polyester sales but hurting profit margins

Bruce F. Greek, C&EN Houston

The ethylene oxide and derivative ethylene glycol businesses are in a slump. Supplies are already excessive and planned additions will bring even more capacity on stream during the next three years or so. Behind the current slump is slow growth in demand, but, as is often the case, consumers of antifreeze, polyester, and other products derived from these chemicals are benefitting from much lower prices.

However, lower prices mean smaller margins and thus lower profitability for producers of these major volume ethylene derivatives. Those in the industry generally expect profitability to remain above the low levels of late 1988 and early 1989.

Most ethylene oxide is consumed captively in making derivatives, especially monoethylene glycol. Merchant sales account for only about 10% of production. Almost 60% of the ethylene oxide produced in the U.S. is converted to the glycol. In addition, diethylene and higher glycols and the various ethoxylates account for almost a quarter of ethylene oxide consumption.

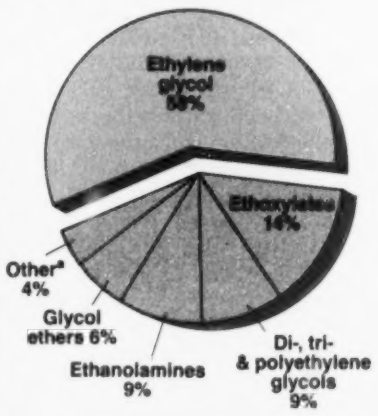
The decline in price for ethylene glycol, to about 25 cents per lb, has caused prices of its main end products—antifreeze and polyesters—to fall, increasing sales of the products this year. The lower prices have carried over into the retail sale of antifreeze. For example, antifreeze prices currently are less than half of those last fall. The demand-price elasticity for ethylene glycol during the past year has been clearly reconfirmed, industry sources say.

Antifreeze sales appear to be following a pattern seen once in the mid-1970s and again in the early 1980s, says David R. Berlin, antifreeze product manager at First Brands Corp., which in 1986 bought the antifreeze business of Union Carbide. During this cycle, Berlin explains, an apparent shortage of antifreeze develops, consumers stock up, prices rise, demand slumps, and then comes a rebound. In 1988, about 216 million gal of antifreeze were sold, which was nearly an all-time high. In 1989, sales fell to less than 161 million gal, according to the annual survey of the Chemical Specialty Manufacturers Association. Preliminary evidence this year indicates that the expected bounceback is under way, Berlin says, but he declines to forecast what 1990 antifreeze sales will total.

Indeed, forecasting output and demand for ethylene oxide and ethylene glycol is difficult for anybody, considering the volatility of domestic demand for antifreeze and exports of ethylene glycol. Most derivatives of ethylene oxide and uses of ethylene glycol are mature products—except for polyester resins used in bottles and other packaging. Consequently, overall growth rates are low. For example, despite high growth rates for polyester bottle resins, the average annual U.S. growth for ethylene glycol between 1989 and 1997 will be only 1.4%, says M. Peter Bellis, vice president of Chemical Marketing Associates Inc., a Houston-based consulting firm.

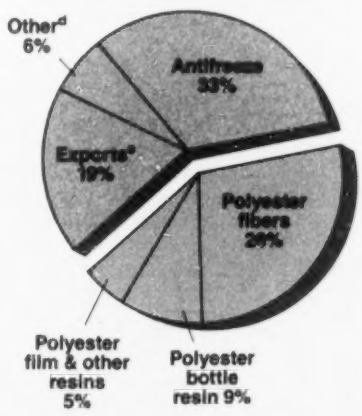
In the company's analysis of ethylene oxide and ethylene glycol markets, growth is forecast to be

Ethylene glycol dominates use of ethylene oxide...



1990 consumption[b] = 6.1 billion lb

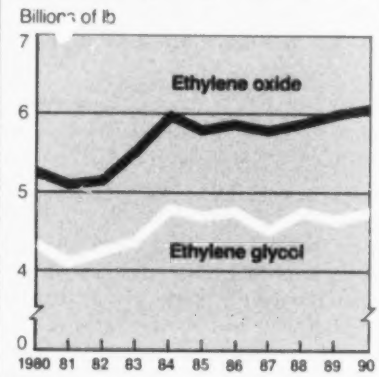
...as polyesters dominate use of ethylene glycol



1990 consumption (including imports)[b] = 5.4 billion lb

a Includes exports, polyether polyols, tetraethylene glycol, as an intermediate in various products, and as a fumigant/sterilant. b Forecast. c Largely fiber-grade for polyesters. d Solvent, alkyd and polyester unsaturated resins, and as an intermediate for various esters and ethers. **Source:** C&EN estimates

Ethylene oxide, ethylene glycol output grows slowly



Sources: U.S. International Trade Commission, C&EN estimates

higher for world demand than for U.S. demand alone. During the period 1989 to 1997, world demand for ethylene oxide is forecast to increase 3.5% annually, and for ethylene glycol 4.1% per year, Bellis says. Polyester fiber uses in the Far East and demand for polyester bottle resins in the U.S. and in Europe will lead the growth.

Polyesters eclipsed antifreeze as the largest use of ethylene glycol in the late 1970s and have continued the fast growth. Combined polyester uses will exceed 42% of U.S. glycol demand this year, including exports. If exports are excluded, polyesters account for 52% of the remaining glycol supply.

Among the polyester uses of ethylene glycol, fibers dominate, at 28% of the total demand this year, or two thirds of all polyester demand. Yet, polyester fiber use is increasing more slowly than all other applications.

Bottles and other packaging uses are the fastest growing uses of polyester. Because of the runup of prices in 1988 and 1989, U.S. consumption of these resins grew little, if any, last year, as competing aluminum producers held prices of can stock and as the development of new applications of these resins lagged.

Various ethoxylates, most of which are used as surfactants, are a distant second as a consumer of ethylene oxide. Examples include ethoxylates of phenol, substituted phenols, linear alcohols, and oils. As a group, these derivatives are expected to increase their demand for ethylene oxide at 2.5 to 3% annually, says Wayne H. Peters, business manager for ethylene oxide and derivatives at Shell Chemical. Demand for these and other ethoxylates used as surfactants in detergent formulations will change little, which makes this use aptly fit the definition of a mature end use of ethylene oxide.

Most other uses of ethylene oxide also will grow at about these same rates, says Peters. The derivatives with slowly increasing demand and those made in significant volumes include various ethanolamines, diethylene and higher glycols, and polyols. Glycol ethers are an exception to such growth. Most of these ethers are used as solvents, especially for coatings. Concerns over the emissions and toxicity of some of the ethers, such as ethyl and propyl, are slowly reducing their annual growth to 1 to 2%. Small miscellaneous uses as a group will grow faster, but the effect on total demand is meager.

Demand growth for ethylene oxide this year likely will exceed the capacity added in 1989 through process improvements, thereby helping the average plant operating rate. Demand likely will grow about 100 million lb to 6.1 billion lb, and capacity will be up about 75 million lb to more than 7.2 billion lb. Thus, the average operating rate will rise only slightly from the 84% of nameplate capacity in 1989.

In the future, significant additional ethylene oxide capacity will start up in both the U.S. and Canada. By 1993, U.S. capacity will be more than 8.3 billion lb and Canadian capacity more than 1.4 billion lb, for a combined total of 9.7 billion lb, according to estimates of Marilyn Bradshaw, project leader at Colin A. Houston & Associates, a consulting firm located in Mamaroneck, N.Y. That represents an increase of more than 1.1 billion lb, or 16%, in the U.S., and 600 million lb, or 48%, in Canada from current capacity totals.

The 1993 capacity totals include announced expansions but don't include forecasts for additions achieved through process improvements. Such improvements can add as much as 3 to 5% per year to capacity for products in strong demand, but, if demand for ethylene oxide and ethylene glycol grows as slowly as forecast, these minor additions will be smaller—about what they were in 1989. Also, with the slow demand growth, the industry can expect excess capacity to continue well into the future. □

Ethylene oxide capacity to jump by 1993

Millions of lb	Location	Capacity 1989	1990	1993
U.S.		7140	7215	8350
BASF	Geismar, La.	480	480	480
Dow Chemical	Plaquemine, La.	500	500	500
Hoechst Celanese	Clear Lake, Tex.	550	550	550
Occidental	Bayport, Tex.	570	600	675
Olin	Brandenburg, Ky.	110	110	110
PD Glycol	Beaumont, Tex.	530	530	620
Quantum	Morris, Ill.	220	220	220
Shell	Geismar, La.	825	870	870
Shell (expansion)	Site undisclosed	—	—	450
Sun	Claymont, Del.	110	110	110
Texaco	Port Neches, Tex.	890	890	1000
Texas Eastman	Longview, Tex.	210	210	210
Union Carbide	Seadrift, Tex.	825	825	825
	Taft, La.	1320	1320	1730
CANADA		960	960	1620
Dow Canada	Ft. Saskatchewan, Alberta	405	405	505
Union Carbide	Prentiss, Alberta	400	400	960[a]
	Montreal, Quebec	155	155	155
TOTAL		8100	8175	9970

a May be built in stages; actual completion date undefined. **Sources:** Colin A. Houston & Associates, C&EN estimates